UDC 666.3.022.66

DEPENDENCE OF CASTING PROPERTIES OF CERAMIC SLIPS ON WATER HARDNESS

N. S. Yugai[1]

Translated from Steklo i Keramika, No. 3, pp. 14 – 18, March, 2005.

It is established that the casting properties of majolica slip depend on the water hardness, the concentration of the electrolyte, and the type of argillaceous component in the ceramic mixture. An increase in water hardness leads to an inevitable increase in the content of electrolyte and the moisture of slip. The casting properties of slip can be stabilized by using water of constant hardness and by monitoring additional parameters.

Control over the casting properties of slips is a critical factor in the technology of ceramics in which the slip-cast method prevails over plastic molding, for instance, in producing fancy ceramics.

It is known that a slip constitutes a homogeneous system consisting of clay – water-electrolyte or ceramic mixture – water – electrolyte. The optimum cast properties of slip (fluidity, viscosity, structuring coefficient) are achieved by introducing various electrolytes whose quantity depends on the nature of the argillaceous component and the type of electrolyte. Traditionally the industry uses waterglass and soda ash as electrolytes. It should be noted that ceramic factories have accumulated vast experience in controlling the flow properties and moisture of porcelain slips using electrolytes of organic origin. Thus, by introducing organic electrolytes one can significantly lower the moisture of a porcelain slip; however, due to interaction between the solid phase and the disperse medium in the slip under the effect of additives, the quality of cast preforms deteriorates. Therefore, organic electrolytes have not gained wide application in factories.

Some studies, including research of the NIIF Institute intended to lowering the moisture of the porcelain slip, have considered the dependence of the flow properties of slip on water hardness. The results of these studies indicate that using water of enhanced hardness requires an increased concentration of traditional electrolytes in porcelain slip.

It is known that slip for majolica is prepared based on low-melting montmorillonite-type clays whose deposits are located near ceramic factories. The working moisture of a slip for casting majolica products exceeds the moisture of a porcelain slip, which calls for additional technological operations for drying gypsum molds and cast preforms.

[1] Gzhel' State Art-Industrial Institute, Gus-Khrustalny, Vladimir Region, Russia.

The present study considers the effect of water hardness and dispersion of clay on the casting properties of majolica slip.

For our study we selected an industrial majolica slip used at the Gzhel' JSC of moisture 52% and the following composition (here and elsewhere, wt.%): 60 Gzhel'skoe deposit clays, 20 clay from the Chasov-Yarskoe deposit, 15 quartz sand, and 5 nepheline-sienite.

It has been observed at the Gzhel' Company that under seasonal variations, especially under winter – spring fluctuations the concentration of electrolyte introduced in the composition of majolica slip needs to be adjusted. Furthermore, the heterogeneous chemical and mineralogical composition and the narrow liquefying interval of Gzhel'skoe clays create substantial difficulties in reaching the optimum casting properties of majolica ceramic mixtures and cause an increased amount of defects in products.

Analysis of studies of low-melting clays from the Gzhel'skoe deposit [1] indicates that the technological properties of majolica mixtures to a great extent depends on the type of clays. For this purpose, Gzhel'skoe clay samples of different tints were selected: variegated, gray-green, and lilac clays.

The degree of dispersion of Gzhel'skoe clays and experimental ceramic mixtures (Table 1) were determined on a Frietsch photosedimentograph (Figs. 1 and 2). Analysis of the granulometric composition of Gzhel'skoe clay samples established their different degrees of dispersion. The highest content of fine particles of size below 1 μm was found in variegated clay (46%), in gray-green clay it was 42%, and in lilac clay 38%, The maximum amount of coarse particles was found in lilac clay — 16.0%, in gray-green it was 14.5%, and in variegated clay 12.5%.

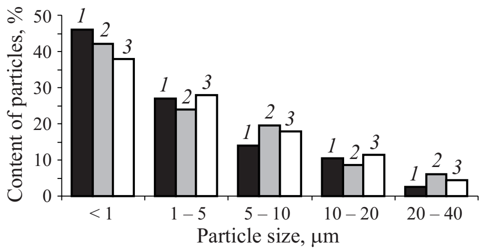

Fig. 1. Histogram of particle distribution in clays from the Gzhel'skoe deposit: *1*, *2*, and *3*) variegated, gray-green, and lilac clay, respectively.

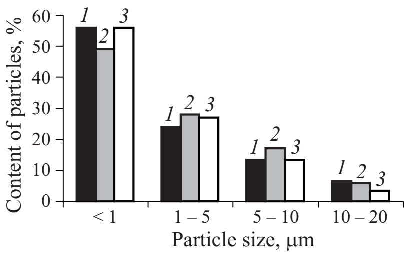

Fig. 2. Histogram of particle distribution in majolica mixtures 16-b (*1*), 27-b (*2*), and 35-a (*3*).

Ceramic mixtures were prepared from these clays according to the traditional scheme: joint moist grinding of the initial components in a ball mill to a residue of 1 – 2% on a No. 0056 sieve.

The dispersion of the experimental mixtures revealed the highest content of particles of size 1 – 10 μm and the lowest (49%) content of finely dispersed particles in mixture 27-b. The granulometric composition of mixtures 16-b and 35-a was virtually identical, except for the content of particles of size 10 – 20 μm (the difference was 3%).

A preliminary estimate of the liquescence of clays and mixtures was made based on their adsorption capacity, i.e., by determining the adsorption capacity of clays based on methylene blue [2]. Thus, the adsorption (mg/g) of clays from the Gzhel'skoe deposit was equal to: 72.0 for variegated, 66.5 for gray-green, and 61.0 for lilac; that of experimental mixtures: 72.0 for 16-b, 72.0 for 27-b, 66.5 for 35-a, and 66.5 for the mixture produced at the Gzhel' Company. The maximum adsorption capacity, equal to 72.0 mg/g, was

TABLE 1

Mixture	Mass content, %					
	variegated clay	gray-green clay	lilac clay	Chasov-Yarskoe clay	quartz sand	nepheline-sienite
16-b	60	30	10	–	–	–
27-b	70	10	20	–	–	–
35-a	60	10	30	–	–	–
Gzhel' Company	60	–	–	20	15	5

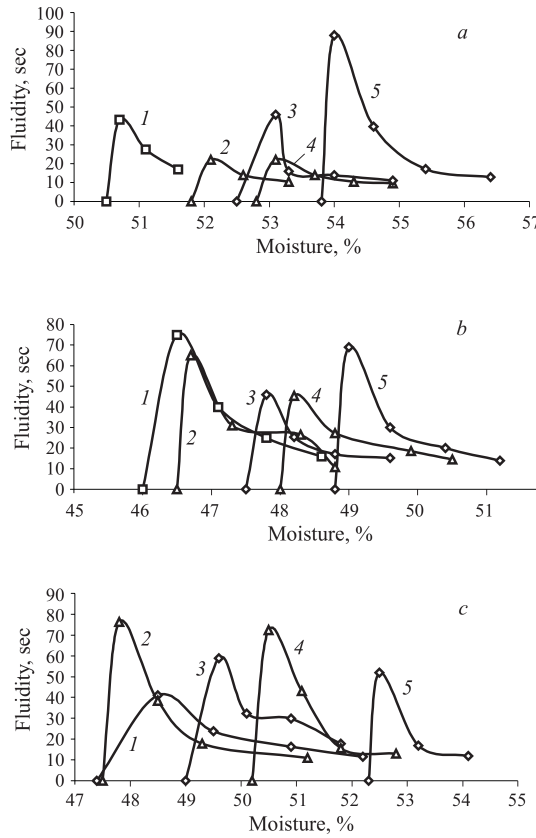

Fig. 3. Dilution of variegated (*a*), lilac (*b*), and gray-green (*c*) clays from Gzhel'skoe deposit using water of different hardness: *1*, *2*, *3*, *4*, and *5*) water hardness 0, 4.5, 5.7, 11.0, and 29.9 mg · equ/liter, respectively.

found in variegated clay and mixtures 16-b and 27-b, and the minimum capacity was found in lilac clay (61.0 mg/g). The results of adsorption measurements suggest that lilac clay and the ceramic mixture based on this clay (35-a) can be classified as easily liquefiable.

The liquescence of Gzhel'skoe clays and ceramics mixtures was determined using the standard method [3] with the introduction of water of different hardness (0, 4.5, 11.0, and 29.9 mg · equ/liter) into suspensions (water taken from different sources in the Gzhel' District). It should be noted that with distilled water the thinning of the variegated clay occurred at a moisture of 51.6%, and the thinning of gray-green and lilac clays at a moisture of 48.6 and 52.2%; as the water hardness increased from 4.5 to 29.9 mg · equ/liter, the liquefying of all clays occurred under a higher moisture. Thus, the variegated clay was thinned under a moisture of 52.6 – 56.4% and gray-green and lilac clays at a moisture of 51.2 and 54.1% (Fig. 3).

Thus, the results of measuring liquescence of different clays from the Gzhel'skoe deposit show that increase in water hardness observed in seasonal fluctuations inevitably leads to an increased moisture of majolica slip. At the same time, the behavior of particular Gzhel'skoe clays was identi-

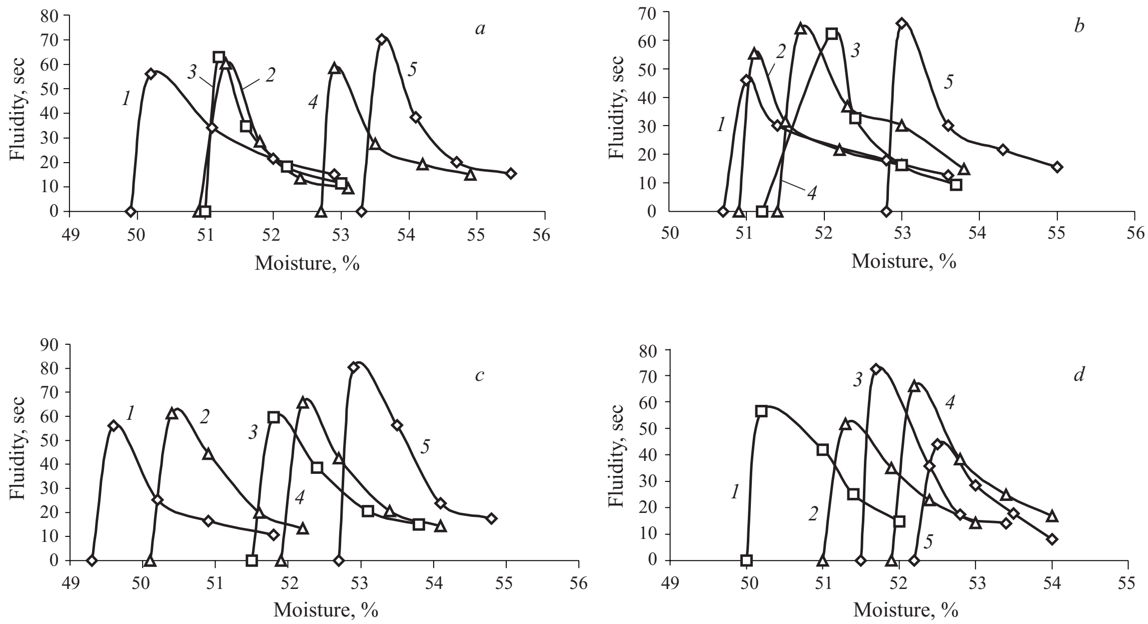

Fig. 4. Dilution of mixtures 16-b (*a*), 27-b (*b*), 35-a (*c*), and mixture from the Gzhel' Company (*d*) using water of different hardness: *1 – 5*) the same as in Fig. 3.

fied: the most liquefiable is lilac clay, next gray-green clay, and finally variegated clay.

The dilution of ceramic mixtures considered was implemented using the same technological scheme. The results of the experiments (Fig. 4) show that the mobility of mixtures with increased water hardness can be achieved only by raising the moisture of all mixtures. Furthermore, for the same hardness of water the moisture of a mixture depends on its composition. For instance, the emergence of the first drop in mixtures 16-b, 27-b, and 35-a diluted by distilled water corresponds to the moisture of 49.9, 50.7, and 49.3%, respectively; as the water hardness changes (29.9 mg · equ/liter), the moisture of the mixtures changes in the same order as in using distilled water and is equal to 53.4, 53.0, and 52.9%, respectively.

However, the thinning of mixture 16-b indicates that within the water hardness interval of 4.5 – 5.7 mg · equ/liter the moisture of the mixture remains steady, although only increase in water hardness increases the moisture of the suspension imparting the required casting properties to the slip. The specifics of the liquescence of mixture 27-b was observed in the water hardness interval of 0 – 11 mg · equ/liter, i.e., the variation in this parameter had no effect on the moisture of the mixture, in fact thinning was achieved with a nearly constant moisture (50.7 – 51.4%). The results of liquefying mixture 35-a corroborated the need to raise the moisture of the mixture as water hardness increases, in order to ensure the required fluidity of the suspension.

The behavior of the industrial majolica mixture produced at the Gzhel' Company differs from the behavior of the experimental mixtures, since its liquefying occurs at a lower moisture of the slip. Its higher capability of dilution compared to the experimental mixtures can be attributed to the presence of grog materials in the batch, whose content is equal to 20% and a decreased content of argillaceous materials.

A comparison of liquefying of experimental mixtures using water of different degrees of hardness shows that mixture 35-a is the most liquefiable, since the emergence of the first drop is registered under the lowest moisture (49%) in contrast to the other mixtures. Furthermore, the maximum mixture moisture equal to 52.8 – 53.2% was registered for all mixtures diluted with water of the maximum hardness (29.9 mg · equ/liter). The results of thinning the experimental mixtures based on Gzhel'skoe clays correlate with the results of thinning corresponding clay samples (variagated, gray-green, and lilac).

The study of the effect of water hardness on the content of electrolytes according to the method in [3] indicates that water hardness not only complicates the casting process due to the increased moisture of the slip, but also has a negative effect on its flow properties. In particular, thixotropic phenomena were identified on introducing a small quantity of electrolytes in the slip. All experimental slips containing water of the maximum hardness (29 mg · equ/liter) exhibited thixotropic properties even when the amount of electrolyte introduced was significantly lower (0.10 – 0.14%) than that of slips prepared with distilled water, where the electrolyte content was up to 0.2%. Moreover, for the same water hardness (11 mg · equ/liter) the most narrow liquescence interval among the slips based on Gzhel'skoe clays was registered in the slip based on the gray-green clay (Fig. 5).

To determine the rheological properties, we used majolica slip containing both waterglass and soda ash. The introduction of electrolytes was varied in sich a way as to produce

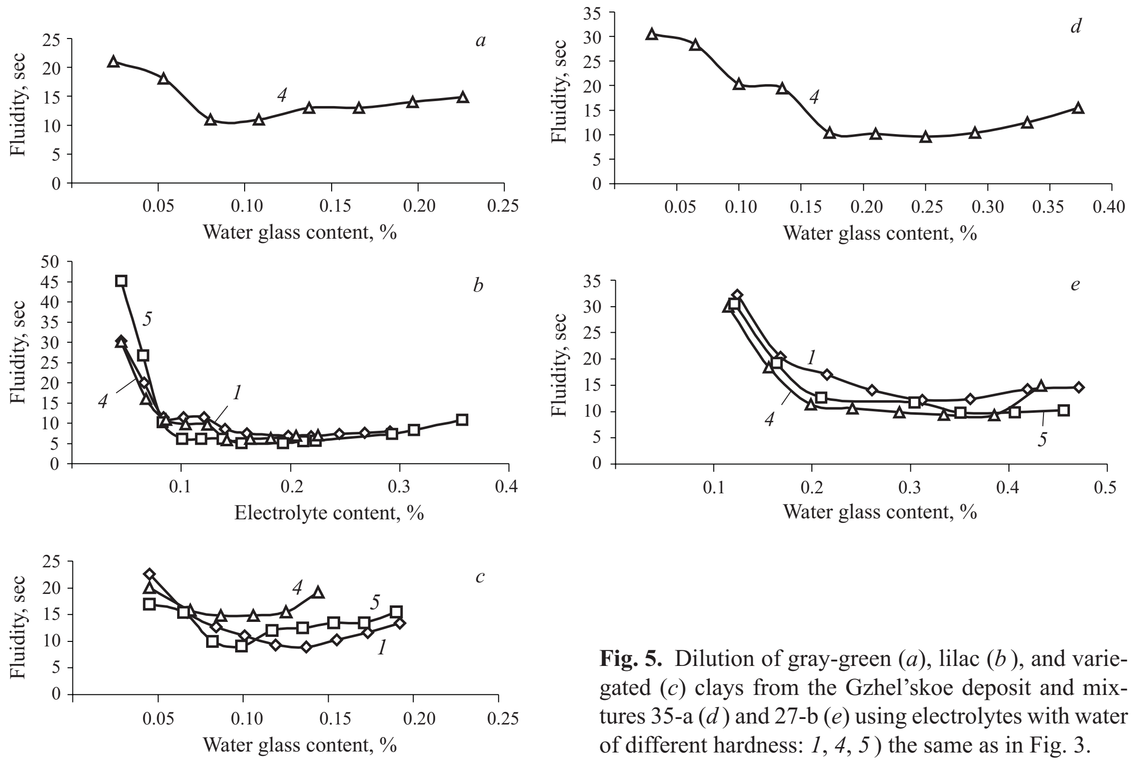

Fig. 5. Dilution of gray-green (*a*), lilac (*b*), and variegated (*c*) clays from the Gzhel'skoe deposit and mixtures 35-a (*d*) and 27-b (*e*) using electrolytes with water of different hardness: *1*, *4*, *5*) the same as in Fig. 3.

slips of various flow properties ensuring good quality of finished products. The results (Table 2) show that the thickening coefficient of slips depends on the content of electrolyte and the hardness of water.

The optimum values of the thickening coefficients of slips were estimated based on the quality of cast preforms after casting and drying. Thus, for slip made of pure clays the optimum values amounted to 1.1 – 1.2 and 2.2, for experimental mixtures they were 1.1 and 1.7. It should be noted that articles products made of slip based on lilac clay exhibited cracks after drying.

The content of electrolytes (waterglass and soda ash) in experimental slip 35-a was lower by 0.14 and 0.07%, respectively than in the industrial majolica slip, whereas the mois-

TABLE 2

Clay or mixture	Slip moisture, %	Water hardness, mg · equ/liter	Electrolyte content, %		Fluidity, sec	Thickening coefficient	Casting duration, sec	Technical and qualitative parameters of experiments products	
			water glass	soda ash				wall thickness, mm	existence of cracks in products
Variegated	51.3	0	0.067	0.015	15.5	2.2	45	2.25	None
	51.8	11.0	0.067	0.010	12.4	1.1	68	3.20	Exist
	50.4	11.0	0.150	0.050	12.5	1.3	47	2.25	None
	51.6	29.9	0.067	0.030	11.5	1.5	66	4.25	Exist
	53.5	29.9	0.125	0.035	14.1	1.7	58	3.90	The same
	51.5	29.9	0.100	0.050	8.9	1.2	54	2.30	None
Lilac	46.0	0	0.045	0.020	10.4	1.2	30	2.50	Exist
	46.4	0	0.083	0.020	9.6	1.5	53	3.00	The same
	44.9	11.0	0.030	0.015	12.6	1.2	60	3.50	″
	45.4	11.0	0.050	0.030	10.8	1.1	48	3.30	″
	46.3	11.0	0.060	0.030	11.0	1.6	50	3.30	″
	44.1	11.0	0.104	0.040	16.6	1.8	60	2.80	″
Lilac	44.9	11.0	0.104	0.052	16.8	2.0	60	3.30	″
Mixture:									
27-b	50.7	11.0	0.100	0.050	11.0	1.1	30	2.60 – 4.30	None
35-a	50.0	11.0	0.060	0.030	14.7	1.1	30	2.50	The same
35-a	51.1	11.0	0.300	0.150	17.6	1.7	30	3.70	″

ture of the experimental slip was lower by 5%. The majolica products cast from slip 35-a had satisfactory quality.

Thus, the flow properties of majolica slip depend on the type of argillaceous component in the ceramic mixture, water hardness, and the concentration of electrolytes.

The hardness of water has a direct effect on the moisture of majolica slip regardless of its composition. The optimum properties of slip in the case of increased water hardness are attained under increased moisture and electrolyte content. An increase in the hardness of water and the content of electrolyte in the slip also affects the liquescence interval, which leads to thixotropic phenomena.

The liquescence of clays and majolica mixtures depends not only on water hardness, but also on the type of clay contained in slips. Gzhel'skoe lilac clay belongs to the easily liquefying type, but it cannot be used for casting high-quality products due to the formation of cracks in products after drying.

It can be stated that monitoring of moisture and the thickening coefficient in the course of casting is insufficient, as the quality of preforms differs even for the same thickening coefficient values. Therefore, such parameters as slip viscosity acquires significance and has to be monitored in casting majolica articles.

To achieve stable flow properties in majolica slips one should use softened water and monitor the constancy of water hardness.

REFERENCES

1. V. M. Loginov and N. S. Yugai, "Low-melting clays from Gzhel'skoe deposit," *Steklo Keram.*, No. 7, 27 – 29 (1999).
2. I. Ya. Yurchak, A. I. Avgustinik, A. S. Zaporozhets, et al., *Research and Control Methods in Porcelain and Faience Production* [in Russian], Moscow (1971).
3. E. S. Lukin and N. T. Andrianov, *Technical Analysis and Control of Ceramic Production* [in Russian], Moscow (1986).